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PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS/STUDENTS REPORTS

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"Surface Chemistry and Structure Studies of  
MBE-Grown Semiconductors and Superconductors"

The Pennsylvania State University

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May, 1991

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## Part I

### a. Papers Submitted to Refereed Journals (and not yet published)

K. Caffey, R. Blumenthal, J. Burnham, E. Furman and N. Winograd, "Arsenic Coverage Dependence of the Angular Distribution of Secondary Ions Desorbed from the GaAs(100) (2x4) Surface", *J. Vac. Sci. Tech. B* (1991), in press.

D. M. Hrubowchak, M. H. Ervin, M. C. Wood and N. Winograd, "Detection of Biomolecules on Surfaces Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", *Anal. Chem.*, (1991), submitted.

R. Blumenthal, K. P. Caffey, E. Furman, B. J. Garrison and N. Winograd, "The Angular Distribution of Ga<sup>+</sup> Ions Desorbed by 3 keV Ion Bombardment of GaAs{001} (2x4)", *Phys. Rev. B*, (1991), in press.

N. Winograd, M. El-Maazawi, R. Maboudian, Z. Postawa, D. N. Bernardo and B. J. Garrison, "Energy- and Angle-Resolved Measurements of Rh(<sup>4</sup>F<sub>9/2</sub>) and Rh(<sup>4</sup>F<sub>7/2</sub>) Populations from Ion-Bombarded Rh{100}", *Phys. Rev. Lett.*, (1991), submitted.

G. P. Malafsky and N. Winograd, "Primary Ion Energy Effect on the Energy and Angular Distributions of Rh<sup>+</sup> Ions Ejected from Rh{111}", *Surf. Sci.* (1991), submitted.

### b. Papers Published in Refereed Journals

J. P. Baxter, G. A. Schick, J. Subbiah-Singh, P. H. Kobrin and N. Winograd, "Angular Distributions of Sputtered Particles", *J. Vac. Sci. Tech.* **3**, 1218 (1986).

G. A. Schick, J. P. Baxter, J. Singh, P. H. Kobrin and N. Winograd, "Multi-Photon Resonance Ionization of Emitted Particles", in *Secondary Ion Mass Spectrometry-SIMS V*, Springer Series in *Chemical Physics* **44**, 90 (1986).

D. W. Moon, R. J. Bleiler, C. C. Chang and N. Winograd, "Energy and Angle-Resolved SIMS Studies of Cl<sub>2</sub> Adsorption on Ag{110}; Evidence for Coverage Dependent Electronic Structure Rearrangement", in *Secondary Ion Mass Spectrometry-SIMS V*, Springer Series in *Chemical Physics* **44**, 225 (1986).

E. White, L. A. DeLouise and N. Winograd, "SIMS/XPS Studies of Surface Reactions on Rh(111) and Rh(331)", in *Secondary Ion Mass Spectrometry-SIMS V*, Springer Series in *Chemical Physics* **44**, 219 (1986).

P. H. Kobrin, G. A. Schick, J. P. Baxter and N. Winograd, "A Detector for Measuring Energy- and Angle-Resolved Neutral-Particle (EARN) Distributions for Material Desorbed from Bombarded Surfaces", *Rev. Sci. Instru.* **57**, 1354 (1986).

M. P. Kaminsky, N. Winograd, G. L. Geoffroy and M. A. Vannice, "Direct SIMS Observation of Methylidyne, Methylidene and Methyl Intermediates on a Ni(111) Methanation Catalyst", *J. Am. Chem. Soc.* **108**, 1315 (1986).

D. W. Moon, R. J. Bleiler and N. Winograd, "Coverage Dependent Structural Changes During Chlorine Adsorption on Ag{110}", *J. Chem. Phys.* **85**, 1097 (1986).

N. Winograd, P. H. Kobrin, G. A. Schick, J. Singh, J. P. Baxter and B. J. Garrison, "Energy and Angle-Resolved Detection of Neutrals Desorbed from Ion Bombarded Single Crystals. Rh{111} and p(2x2)O/Rh{111}", *Surf. Sci. Lett.* **176**, L817 (1986).

E. J. Karwacki and N. Winograd, "A SIMS Study of the Catalytic Oxidation of Methanol on Cu{110}", *J. Vac. Sci. Tech.* **4**, 1433 (1986).

J. P. Baxter, J. Singh, G. A. Schick, P. H. Kobrin, and N. Winograd, "Energy and Angle-Resolved Studies of Neutrals Desorbed from Ion Bombarded Polycrystalline Metal Surfaces", *Nuclear Instrum. and Methods B.*, **B17**, 300 (1986).

B. I. Craig, J. P. Baxter, J. Singh, G. A. Schick, P. H. Kobrin, N. Winograd, and B. J. Garrison, "Deexcitation Model for sputtered Neutral Atoms", *Phys. Rev. Lett.* **57**, 1351 (1986).

B. J. Garrison, N. Winograd, D. Lo, T. A. Tombrello, M. H. Shapiro, and D. E. Harrison, Jr., "Energy Cost to Sputter an Atom from a Surface in keV Ion Bombardment Processes", *Surface Sci.* **180**, L129 (1987).

N. Winograd, "Surface Studies Using Particle Beam Induced Desorption and Multiphoton Resonance Ionization", *Resonance Ionization Spectroscopy*, Institute of Physics Conference Series Number **84**, 1987, page 145.

J. Singh, C. T. Reimann, J. P. Baxter, G. A. Schick, P. H. Kobrin, B. J. Garrison, and N. Winograd, "Detection of Neutral Atoms Sputtered from Ion-Bombarded Single Crystals Rh{111} and p(2x2) O/Rh{111}: Ejection Mechanisms and Surface Structure Determinations from Energy- and Angle-Resolved Measurements", *J. Vac. Sci. Tech. A* **5**, 1191 (1987).

C. C. Chang, G. P. Malafsky, and N. Winograd, "Shadow-cone Enhanced Desorption with Angle-Resolved SIMS Detection", *J. Vac. Sci. Tech. A* **5**, 981 (1987).

D. Y. Lo, M. H. Shapiro, T. A. Tombrello, B. J. Garrison, and N. Winograd, "Simulation Studies of Collision Cascades in Liquid Targets", *Proceedings of Materials Research Society Meeting* **74**, 449 (1987).

B. J. Garrison, C. T. Reimann, N. Winograd, and D. E. Harrison, Jr., "Energy and Angular Distributions of Rh Atoms Ejected due to Ion Bombardment from Rh{111}: A Theoretical Study", *Phys. Rev.* **B36**, 3516 (1987).

R. Levis, N. Winograd and L. A. DeLouise, "The Influence of Surface Atomic Steps on Site-Selective Adsorption Processes. Ethylidyne Formation on Rh{111} and Rh{331}", *J. Am. Chem. Soc.* **109**, 6873 (1987).

B. J. Garrison, N. Winograd, D. M. Deaven, C. T. Reimann, D. Y. Lo, T. A. Tombrello, D. E. Harrison, Jr. and M. H. Shapiro, "Many-body Embedded-Atom Potential for Describing the Energy and Angular Distributions of Rh Atoms Desorbed from Ion-Bombarded Rh{111}", *Phys. Rev.* **B37**, 7197 (1988).

B. J. Garrison, N. Winograd, D. M. Deaven, C. T. Reimann, D. Y. Lo, T. A. Tombrello, D. E. Harrison, Jr. and M. H. Shapiro, "Many-body Interactions for Theoretical Studies of KeV Particle Bombardment", in *Secondary Ion Mass Spectrometry (SIMS VI)*, John Wiley and Sons, New York, 1988, page 37.

C. T. Reimann, K. Walzl, M. El-Maazawi, B. J. Garrison, and N. Winograd, "The Effect of Adsorbates on the Angular Patterns of Ion-Induced Rh Atom Ejection from Rh{111}: Surface Structure Determinations", in *Secondary Ion Mass Spectrometry (SIMS VI)*. John Wiley and Sons, New York, 1988, page 1037.

R. J. Levis, Z. C. Jiang, and N. Winograd, "An Ultrahigh Vacuum Study of the Production of Methanol on Pd{111}", in *Secondary Ion Mass Spectrometry (SIMS VI)*, John Wiley and Sons, New York, 1988, page 1045.

D. Y. Lo, T. A. Tombrello, M. H. Shapiro, B. J. Garrison, N. Winograd and D. E. Harrison, Jr., "Theoretical Studies of Ion Bombardment: Many-Body Interactions", *J. Vac. Sci. Tech. A* **6**(3), 708 (1988).

C. C. Chang, N. Winograd and B. J. Garrison, "Model Studies of Particle/Solid Interactions", *Surface Sci* **202**, 309 (1988).

G. P. Malafsky and N. Winograd, "Transport Optics for a Space Charge Broadening Ion Beam", *Rev. Sci. Instru.* **59**, 1294 (1988).

R. J. Levis, J. Zhicheng and N. Winograd, "Evidence for Activation of the C-O Bond of Methanol on the Pd{111} Surface after Low Temperature Adsorption", *J. Am. Chem. Soc.* **110**, 4431 (1988).

Rik Blumenthal, S. K. Donner, J. L. Herman, Rajender Trehan, K. P. Caffey, B. D. Weaver, Ehud Furman and Nicholas Winograd, "Secondary Ion Mass Spectroscopic Studies of the Atomic Geometry of GaAs(110)", *J. Vac. Sci. Tech. B* **6**, 1444 (1988).

C. T. Reimann, K. Walzl, M. El-Maazawi, D. M. Deaven, B. J. Garrison, and N. Winograd, "KeV Ar-Ion-Induced Neutral Atom Desorption from Rh{331}: Relation of Angular Distributions Surface Structure", *J. Chem. Phys.* **89**, 2539 (1988).

D. L. Pappas, N. Winograd, and F. M. Kimock, "Characterization of Atoms Desorbed From Surfaces By Energetic Ion Bombardment Using Multiphoton Ionization Detection", in *The Handbook of Ion Beam Processing Technology*, J. J. Cuomo, S. M. Rossnagel and H. R. Kaufmann, Eds., Noyes Publications, Park Ridge, New Jersey, 1988, page 128.

D. M. Hrubowchak, D. L. Pappas, M. H. Ervin, L. Mitchell, and N. Winograd, "Detection of Trace Levels of Radioactive Decay. Is It Possible to Determine Beta-Beta Decay Half-Lives?" in *Resonance Ionization Spectroscopy*, Institute of Physics Conference Series Number **94**, 1988, page 357.

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- N. Winograd and C.-C. Chang, "Coverage-Dependent Bond-Length Changes of Chlorine Adsorbed on Ag{110} Determined by Shadow-Cone Enhanced Desorption", *Phys. Rev. Lett.* **62**(21), 2568 (1989).
- R. J. Levis, J. Zhicheng and N. Winograd, "The Thermal Decomposition of  $\text{CH}_3\text{OH}$  Adsorbed on Pd{111}: A New Reaction Pathway Involving  $\text{CH}_3$  Formation", *J. Am. Chem. Soc.* **111**, 4605 (1989).
- S. K. Donner, J. L. Herman, Rik Blumenthal, R. Trehan, Ehud Furman and N. Winograd, "Growth of Al on GaAs(100): Observation of Interfacial Submonolayer Structure", *App. Phys. Lett.* **15**, 1753 (1989).
- S. K. Donner, K. P. Caffey and N. Winograd, "Effect of Disorder on the Al/GaAs Interface", *J. Vac. Sci. Tech. B* **7**(4), 742 (1989).
- B. J. Garrison, K. Walzl, M. El-Maazawi, N. Winograd, C. T. Reimann and D. M. Deaven, "A Many-Body Embedded Atom Potential For Describing Ejection of Atoms from Surfaces", *Rad. Effects and Defects in Solids* **109**(1-4), 287 (1989).
- B. D. Weaver, D. R. Frankl, Rik Blumenthal and N. Winograd, "Atom-Scattering Study of  $\text{Ar}^+$  Ion Damaged GaAs(110)", *Surf. Sci.* **222**, 464 (1989).
- R. J. Levis, L. A. DeLouise, E. J. White and N. Winograd, "Defect Induced Surface Chemistry: A Comparison of the Adsorption and Thermal Decomposition of  $\text{C}_2\text{H}_4$  of Rh{111} and Rh{331}" *Surf. Sci.* **230**, 35 (1990).
- B. J. Garrison and N. Winograd, "Don E. Harrison, Jr. A Retrospective and Prospective", in *Secondary Ion Mass Spectrometry (SIMS VII)*, A. Benninghoven, C. A. Evans, K. D. McKeegan, H. A. Storms and H. W. Werner, Eds., John Wiley and Sons, New York, 1989, page 1.
- C.-C. Chang and N. Winograd, "Surface Bond-Length Determinations with Shadow-Cone Enhanced Desorption", in *Secondary Ion Mass Spectrometry (SIMS VII)*, A. Benninghoven, C. A. Evans, K. D. McKeegan, H. A. Storms and H. W. Werner, Eds., John Wiley and Sons, New York, 1989, page 33.
- R. Blumenthal, K. P. Caffey and N. Winograd, "The Ion Induced Angular Distribution Patterns of GaAs(110) and Al/GaAs(110)", in *Secondary Ion Mass Spectrometry (SIMS VII)*, A. Benninghoven, C. A. Evans, K. D. McKeegan, H. A. Storms and H. W. Werner, Eds., John Wiley and Sons, New York, 1989, page 57.
- G. P. Malafsky and N. Winograd, "The Influence of Megaevent Collision Sequences on Secondary Ionization", in *Secondary Ion Mass Spectrometry (SIMS VII)*, A. Benninghoven, C. A. Evans, K. D. McKeegan, H. A. Storms and H. W. Werner, Eds., John Wiley and Sons, New York, 1989, page 37.
- D. M. Hrubowchak, M. H. Ervin and N. Winograd, "What are the Limits of Detection for Molecules on Surfaces Using Ion Beam Induced Desorption?", in *Secondary Ion Mass Spectrometry (SIMS VII)*, A. Benninghoven, C. A. Evans, K. D. McKeegan, H. A. Storms and H. W. Werner, Eds., John Wiley and Sons, New York, 1989, page 805.

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R. Maboudian, M. El-Maazawi, Z. Postawa, C. T. Reimann, G. P. Malafsky, D. Hrubowchak, M. Ervin, B. J. Garrison and N. Winograd, "Energy and Angular Distributions of Particles Desorbed From Surfaces Using Multiphoton Resonance Ionization Detection", *SPIE Proceedings* **1208**, 41 (1990).

R. Blumenthal and N. Winograd, "The Angular Distribution of Ga<sup>+</sup> Ions Desorbed by 3 keV Ion Bombardment of GaAs(110)", *Phys. Rev. B* **42**(17), 11 027 (1990).

R. Maboudian, Z. Postawa, M. El-Maazawi, B. J. Garrison and N. Winograd, "Angular Distribution of Rh Atoms Desorbed from Ion-Bombarded Rh(100): Effect of Local Environment", *Phys. Rev. B* **42**(12), 7311 (1990).

D. M. Hrubowchak, M. H. Ervin and N. Winograd, "Characterization of Polycyclic Aromatic Compounds on Surfaces Using Ion-Beam Induced Desorption and Multiphoton Resonance Ionization", *Anal. Chem.* **63**, 225 (1991).

R. Maboudian, M. El-Maazawi, Z. Postawa and N. Winograd, "Angular and Energy Distributions of Rh Atom Desorbed in an Excited State from Ion-Bombarded Rh(100)", *Proceedings of Materials Research Society Meeting*, (1990).

N. Winograd, D. M. Hrubowchak, M. H. Ervin and M. C. Wood, "Multiphoton Resonance Ionization of Molecules Desorbed from Surfaces by Ion Beams", *SPIE Proceedings*, (1991).

M. H. Ervin, D. M. Hrubowchak, M. C. Wood and N. Winograd, "Surface Sensitive Detection of Organic Molecules Using Ion Beam Induced Desorption", *5th International Symposium on Resonance Ionization Spectroscopy & Its Applications*, (RIS 90), IOP Publishing, (1991), p. 417.

M. El-Maazawi, Z. Postawa, R. Maboudian, B. J. Garrison, and N. Winograd, "Surface Characterization and Adsorbate-Site Determination Using Multiphoton Resonance Ionization Detection of Desorbed Particles", *5th International Symposium on Resonance Ionization Spectroscopy & Its Applications*, (RIS 90), IOP Publishing, (1991), p. 451.

M. El-Maazawi, R. Maboudian, Z. Postawa and N. Winograd, "Energy and Angular Distributions of Excited Rh Atoms Ejected from Rh(100)", *Phys. Rev. B* **43**(14), 12078 (1991).

c. Book Chapter Submitted for Publication

N. Winograd and B. J. Garrison, "Surface Structure and Reaction Studies by Ion-Solid Collisions", in *Methods of Surface Characterization*, Vol. 2, Plenum, New York, (1989), in press.

d. Books or Chapters Published

None

e. Technical Reports etc.

None

f. Patents Filed

None

g. Patents Granted

None

h. Invited Presentations at Topical or Scientific/Technical Society Conferences

Physical Chemistry Colloquium, University of California at Irvine, Irvine, CA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", February 4, 1986.

Physical Science Colloquium, Naval Weapons Center, China Lake, CA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", February 13, 1986.

Physical Chemistry Colloquium, University of California at Los Angeles, Los Angeles, CA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 3, 1986.

Chemistry Colloquium, University of Georgia, Athens, GA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 19, 1986.

Chemistry Colloquium, Georgia Institute of Technology, Atlanta, GA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 20, 1986.

Chemistry Colloquium, University of Florida, Gainesville, FL, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 21, 1986.

Chemistry Colloquium, Emory University, Atlanta, GA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", March 24, 1986.

Physics Colloquium, California Institute of Technology, Pasadena, CA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", May 1, 1986.

Chemistry Colloquium, California State University, Fullerton, CA., "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", May 2, 1986.

Chemistry Colloquium, University of California, Riverside, CA "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", May 7, 1986.

Chemistry Colloquium, Harvard University, Boston, MA, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", May 21, 1986.

Sohio, Cleveland, OH, "Surface Studies Using Ion Beam Induced Desorption and Multiphoton Resonance Ionization", June 19, 1986.

Gordon Conference on Analytical Chemistry, New Hampton, NH, "New Approaches to the Studies of Solids and Surfaces Using Particle Beams", August 11, 1986.

Gordon Conference on Electronic Materials, Concord, NH, "Secondary Neutral Mass Spectrometry", August 21, 1986.

Third International Symposium on Resonance Ionization Spectroscopy and Its Applications, Swansea, UK, "Surface Studies Using Particle Beam Induced Desorption and Multiphoton Resonance Ionization", September 7-12, 1986.

American Vacuum Society, Malibu CA, "Secondary Ion Mass Spectrometry", September 25, 1986.

Akron ACS Award Symposium, Akron, Ohio, "Ion Beam Studies of Solids and Surfaces", October 16, 1986.

University of Akron, Akron, Ohio, "Ion Beam Studies of Solids and Surfaces", October 17, 1986.

University of Wisconsin, Madison, WI, "Multiphoton Resonance Ionization of Particles Desorbed from Surfaces by Ion Bombardment", October 21, 1986.

Eastern Analytical Symposium New York City, NY, "Ion Beam, Lasers and X-Rays! Some Aspects of the Current Renaissance in Surface Science", October 23, 1986.

10<sup>th</sup> International Vacuum Congress, Baltimore, MD, "Energy and Angle Resolved Studies of Sputtered Particles", October 24, 1986.

Vanderbilt University, Nashville, TN, "Energy and Angle Resolved Studies of Sputtered Particles", November 7, 1986.

University of Virginia, Charlottesville, VA, "Ion Beam Studies of Solids and Surfaces", November 21, 1986.

Rensselaer Polytechnic Institute, Troy, NY, "Novel Approaches to the Study of Surface Reactions", December 4, 1986.

Indiana University, Bloomington, IN, "Ion Beam Studies of Solids and Surfaces", December 10, 1986.

American Physical Society, New York City, NY, "Ion Beam/Surface Interaction", March 18, 1987.

University of Houston, Houston, TX, "Surface Studies Using Ion Beams Induced Desorption and Multiphoton Resonance Ionization", March 30, 1987.

University of Texas, Austin, TX, "Surface Studies Using Ion Beams Induced Desorption and Multiphoton Resonance Ionization", April 2, 1987.



Case Western Reserve University, Cleveland, OH, "Surface Chemistry Studies with Ion Beams and Lasers", April 25, 1987.

CLEO/IQEC '87, Baltimore MD, "Surface Studies Using Particle Beam Induced Desorption and Multiphoton Resonance Ionization", April 29, 1987.

Rochester Section ACS, Rochester, NY, "Surface Analysis and Laser Ionization of Sputtered Neutrals", May 13, 1987.

Third Workshop on Biomolecular and Environmental Mass Spectrometry, Laghi di Sibari, ITALY, "Energy and Angle Resolved SIMS", July 20, 1987.

AFOSR Contractors Conference, U.S. Air Force Academy, Colorado Springs, CO, "Surface Characterization and Modification using Energetic Particle Beams.", September 18, 1987.

Chemistry Department Colloquium, Iowa State University, Ames, IO, "Surface Studies with Ion Beams and Lasers", October 22, 1987.

Analytical Chemistry Seminar, Iowa State University, Ames, IO, "Is It Possible to Count Single Atoms on Surfaces?", October 23, 1987.

Lilly Research Laboratories Seminar, Indianapolis, IN, "Ion Beam Studies of Biomolecules", November 16, 1987.

Analytical Science Symposium, Hercules Incorporated Research Center, Wilmington, DE, "Surface Studies Using Ion Beams and Lasers", January 22, 1988.

Lawrence Berkeley Laboratory Seminar, Berkeley, CA, "Surface Studies Using Ion Beams and Lasers", March 16, 1988.

Allied-Signal, Inc., Corporate Technology, Morristown, NJ, "Surface Studies Using Particle Beam Induced Desorption and Multiphoton Resonance Ionization", March 24, 1988.

Fourth International Symposium on Resonance Ionization Spectroscopy and its Applications, Gaithersburg, MD, "Surface Studies using Ion Beams and MPRI", April 12, 1988.

Texas Instruments Technology Day, Dallas, TX, "Texas Instrument Founders Prize Update", May 11, 1988.

ACS Summer Symposium on Lasers in Analytical Chemistry Stanford, CA, "Surface Studies Using Ion Beams and MPRI", June 26-29, 1988.

7<sup>th</sup> International Workshop on Inelastic Ion Surface Collisions, Kraków, Poland, "Energy and Angular Distributions of Desorbed Atoms and Molecules", September 19-23, 1988.

Chemistry Department Colloquium, University of Tennessee, Knoxville, TN, "Surface Studies Using Ion Beams and Lasers", November 3, 1988.

Chemistry Department Colloquium, Oak Ridge National Laboratory, Oak Ridge, TN, "Surface Studies Using Ion Beams and Lasers", November 4, 1988.

Analytical and Physical Chemistry Seminar Series, University of Delaware, Newark, DE, "Surface Studies Using Ion Beams and Lasers", November 14, 1988.

Electrochemistry Gordon Conference, Ventura, CA, "Interaction of Energetic Particles with Solid Surfaces", January 15-20, 1989.

Reilly Award Symposium, Pittsburgh Conference, Atlanta GA, "Perspectives on the Transition from Electrochemistry to Surface Science", March 14, 1989.

Chemistry Department Colloquium, University of Michigan, Ann Arbor, MI, "Surface Chemistry with Ion Beams: Surface Structure and Reaction Intermediates", March 20, 1989.

Chemistry Departmental Colloquium, SUNY-Buffalo, Buffalo, NY, "Surface Chemistry with Ion Beams: Surface Structure and Reaction Intermediates", April 5, 1989.

SIMS VII, Monterey CA, "Don E. Harrison: A Retrospective and Prospective", September 4, 1989.

Amy-Mellon Lecture, Purdue University, "Modern Approaches to Surface Analysis", October 19, 1989.

Frontier Science Lecture, National Science Foundation Chemistry Division Advisory Committee Meeting, "Surface Chemistry with Ion Beams: Surface Structure and Reaction Intermediates", October 26, 1989.

Chemistry Departmental Colloquium, Texas A&M, "Modern Approaches to Surface Analysis", November 1, 1989.

SPIE Lasers 90, Los Angeles, CA, "Energy and Angular Distributions of Atoms and Molecules Desorbed from Surfaces Using Multiphoton Resonance Ionization Detection", January 18, 1990.

Amoco Chemical Company, Naperville, IL, "XPS/SIMS Studies of Methyl Formation on Metal Surfaces", March 12, 1990.

12th Symposium on Applied Surface Analysis, American Vacuum Society, "Trace Analysis of Atoms and Molecules on Surfaces Using Ion Beams", April 25, 1990.

Los Alamos National Laboratory, Los Alamos, NM, "Surface Science with Ion Beams and Laser", April 26, 1990.

ACS National Meeting, Washington, DC, "Multiphoton Resonance Ionization of Molecules Desorbed from Surfaces by Ion Beams", August 30, 1990.

FACSS Meeting "Materials Characterization with Ion Beams and Lasers", October 7-12, 1990.

University of Kaiserslautern, Kaiserslautern, Germany, "Shadow-Cone Enhanced SIMS", September 24, 1990.

University of Kaiserslautern, Kaiserslautern, Germany, "Materials Characterization with Ion Beams and Lasers", September 24, 1990.

FACSS Meeting, Cleveland, OH, "Materials Characterization with Ion Beams and Lasers", October 7-12, 1990.

SPIE Lasers 91, Los Angeles, CA, "Multiphoton Resonance Ionization of Molecules Desorbed from Surfaces by Ion Beams", January 21, 1991.

Chemistry Departmental Colloquium, Cornell University, "Surface Chemistry with Ion Beams and Lasers", January 31, 1991.

Analytical Chemistry Seminar, The Ohio State University, Cleveland, OH, "Surface Chemistry with Ion Beams and Lasers", April 2, 1991.

Fisher Award Symposium at the American Chemical Society National Meeting, Atlanta, GA, "Surface Characterization with Ion Beams and Lasers", April 16, 1991.

Chemistry Department 1991 Academic Awards Ceremony, Case Western Reserve University, Cleveland, OH, April 23, 1991.

39th ASMS Conference on Mass Spectrometry and Allied Topics, Nashville, TN, "Trace Analysis of Atoms and Molecules on Surfaces Using Ion Beams", May 20, 1991.

Third Annual Topical Symposium of the Western Pennsylvania Chapter of the American Vacuum Society, Pittsburgh, PA, "Dynamics of Ion Beams/Solid Interactions", June 3, 1991

Organized "2nd International Workshop on Postionization Techniques in Surface Analysis" held at Penn State University, May 15-17, 1991.

i. Contributed Presentations at Topical or Scientific/Technical Society Conferences

None

j. Honors/Awards/Prizes

The Akron ACS Section Award 1986

American Microchemical Society Bennedetti-Pichler Award, 1991

Outstanding Alumnus Award, Case Western Reserve University, 1991

k. Number of Graduate Students Receiving Full or Partial Support on ONR Contract

Total 11

Minorities 1

Asian 1

Number of Postdoctoral Associates Receiving Full or Partial Support on ONR Contract

Total 4

Minorities 1

Asian 1

## Part II

a. Principal Investigator

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Dr. Mark Ross

d. Brief (100-200 words) Description of Project

This proposal is focused on the basic aspects of the chemistry of epitaxial thin film growth. The experiments stem from the recent construction of a flexible deposition chamber equipped with molecular beam epitaxy (MBE), atomic layer epitaxy (ALE) and migration enhanced epitaxy (MEE). This chamber is linked via a specially designed sample transfer system to a surface analysis system with unique capabilities for examining the chemistry and structure of superlattices and interfaces. These techniques include angle-resolved secondary ion mass spectrometry, x-ray photoelectron spectroscopy, low energy electron diffraction and He-atom diffraction. Our initial experiments will be involved with the study of the structure and chemistry of metal overlayers and interfaces as part of our continuing interest in group III-V materials. Next, we plan a major new expansion of effort to include the capability of synthesizing a variety of group IV semiconductor structures, concentrating mainly on the study of strain in the Ge/Si(100) system. Of special interest will be to compare the surface properties of Si surfaces grown at low temperatures using disilane by ALE to those produced at higher temperatures by MBE or MEE. In general, we plan to correlate the surface structure and chemistry of a variety of complex architecturally designed epitaxial layers with electronic properties to guide in the future fabrication of these novel artificially-synthesized materials.

e. Significant Results During the Contract Period

Please see attached reprints

f. List of Names of Graduate Students and Post-doctorals Currently Working on Project

Graduate Students

Bradley Weaver  
Susan Donner  
Joe Herman  
Dave Hrubowchak  
Jr.-Jyan Chen  
Geoffrey Malafsky  
Mohamed El-Maazawi  
Jay Burnham  
Rob Braun  
Kevin Caffey  
Steven Goss

Post-doctorals

Raj Trehan  
Kerry Walzl  
Curt Reimann  
Roya Maboudian

Reprint Series  
6 January 1989, Volume 243, pp. 64–66

**SCIENCE**

## **Atom Counting at Surfaces**

DAVID L. PAPPAS, DAVID M. HRUBOWCHAK, MATTHEW H. ERVIN,  
AND NICHOLAS WINOGRAD

# Atom Counting at Surfaces

DAVID L. PAPPAS, DAVID M. HRUBOWCHAK, MATTHEW H. ERVIN,  
NICHOLAS WINOGRAD

Multiphoton resonance ionization has been combined with energetic ion bombardment to examine dopant concentrations of indium on the surface of silicon. The results yield a linear relation between the indium concentration and the known bulk values and a detection limit of 9 parts per trillion, at a mass resolution exceeding 160. This measurement, which surpasses the limits of any previous surface analysis by a factor of 100, has been made possible with an experimental configuration that optimizes sampling and detection efficiency while reducing background noise to virtually zero. During the analysis, submonolayer quantities of the surface are removed, so that as few as 180 surface atoms may be counted.

IT IS NOW POSSIBLE TO SPECTROSCOPICALLY detect extremely low concentrations of atoms and molecules in bulk phases. For example, researchers have been able to count single atoms of gaseous cesium diffusing through the path of a laser beam by taking advantage of the detection selectivity and efficiency of multiphoton resonance ionization (MPRI) spectroscopy (1). Similar experiments have allowed the collection of one molecule of gaseous naphthalene out of four present in the ionization volume (2). In solids or liquids, a variety of methodologies such as neutron activation analysis and secondary ion and glow discharge mass spectrometries offer, in special circumstances, exceptional detection limits exceeding one atom in  $10^{12}$  background atoms (3).

The detection of a small number of atoms at solid surfaces has not yet been possible, primarily because of difficulties in efficient sampling of monolayers. We have proposed, however, that a few atoms could be desorbed from the top layer of a solid by means of energetic ion bombardment and that these atoms could be selectively and efficiently detected by MPRI spectroscopy (4). A number of groups have now demonstrated the feasibility of such an approach for the characterization of ultrapure materials, although theoretically attainable detection limits have yet to be achieved (4-7). We report the development of a new apparatus for MPRI studies, featuring a time-of-flight (TOF) reflectron-based detector coupled with a specially designed high-power, pulsed kiloelectron volt, ion bombardment source, which allows mass-resolved detec-

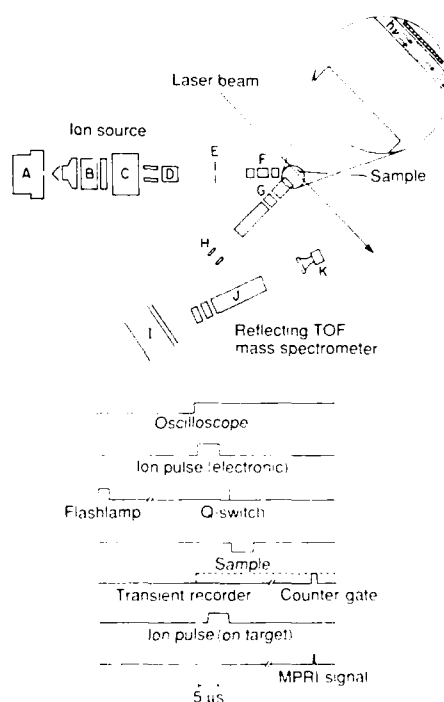
tion of just a few hundred surface atoms. The method has been applied to the study of low concentrations of dopants at semiconductor surfaces.

The experimental system used for these measurements has been described (5, 8). Briefly, a pulsed beam of  $\text{Ar}^+$  ions (5.6  $\mu\text{s}$ , 10 keV) is directed upon the sample at  $45^\circ$  incidence, thereby desorbing some fraction of the surface material. A few hundred nanoseconds later, the frequency-doubled, unfocused output of a neodymium: yttrium-aluminum-garnet pumped dye laser is introduced through the cloud of ejecting particles, resonantly ionizing the neutral species of interest. The photoions are extracted into a TOF mass spectrometer equipped with an ion reflector and are subsequently detected by a dual microchannel plate assembly. Mass spectra are recorded with a 100-MHz transient digitizer, while for the actual analyses single-ion counting is carried out with an amplifier-discriminator coupled to a photon counter-processor. The entire apparatus and experimental timing are shown in Fig. 1. The targets were composed of high-purity silicon (Si), uniformly doped with indium (In) at concentrations of 2 parts per million (ppm), 36.5 parts per billion (ppb), or 3.85 ppb (9). Each wafer was fastened to the manipulator, which was covered with either a sheet of copper (Cu) or Si to serve as a backplate (10).

The desorbed In may be selectively excited in a one-step resonance absorption (304 nm, 0.850 mJ per pulse), followed by ionization with a visible photon (608 nm, 7.03 mJ per pulse). This is a suitable scheme for optimizing the signal-to-noise (S/N) ratio because the power of the highly energetic ultraviolet (UV) photon is kept at a low

level while the powerful visible light is reserved for the more difficult ionization step. To minimize the effects of possible contamination or surface segregation, we sputter-etched the samples before each data acquisition cycle until a steady-state, reproducible signal was obtained. The data were then accumulated for 5 min (9000 laser pulses at a repetition rate of 30 Hz), after which the background signal was measured for an equivalent period. In order to detect single pulses, we attenuated the photoion signal for the two most concentrated samples by reducing the primary ion current. Individual determinations were normalized to the measured ion current and laser power.

The TOF mass spectra for the Si target doped with 2 ppm In are shown in Fig. 2. Because the laser bandwidth is broader than the spectroscopic isotope shifts, the ion reflector is required to resolve the two In isotopes. For comparison, the same time interval was monitored with the laser blocked; the absence of any appreciable sec-



**Fig. 1.** Schematic diagram of the MPRI apparatus (**top**) and experimental timing sequence used for the In in Si experiments (**bottom**): A, duoplasmatron ion source; B, emission lens; C,  $E \times B$  filter (where  $E$  is an electric field and  $B$  is a magnetic field); D, pulse steering plate; E, pulsing aperture; F, refocusing lens; G, extraction lens; H, deflection plates; I, ion reflector; J, lens; and K, microchannel plate detector. Expanded area (top right) shows the overlap region of the unfocused laser beam and the desorbed particles. The sample is held at a high potential during the time that the ion pulse is incident on the target to accelerate the secondary ions to high velocities. This is reduced to the normal extraction voltage (relative to the grounded extraction grid) during the time that the laser is active.

**Table 1.** MPRI experimental data for In in Si.

[In] (ppb)	Average signal*	Average back- ground*	Ar <sup>+</sup> cur- rent ( $\mu$ A)	Laser power (W)	Relative intensity*
2000	$1.45 \times 10^3$	18.5	0.158	0.186	$(4.84 \pm 0.08) \times 10^4$
36.5	$2.78 \times 10^3$	29.5	18.0	0.158	$880 \pm 62.4$
3.85	$9.41 \times 10^2$	9.6	47.3	0.211	$93.7 \pm 22.6$
0.165	$3.72 \times 10^1$	4.0	46.0	0.211	$3.43 \pm 0.58$

\*Signal and background are expressed as counts per 9000 laser pulses, averaged over three analyses. \*Relative intensity is derived by normalizing the data for each individual analysis to the ion current and laser power and obtaining a cumulative average. The results in this column have been used to generate the calibration plot. The error limits are reported at the 95% confidence level from three independent observations.

ondary ion signal over this domain is indicative of the entire spectrum and is the result of the energy-discriminating capacity of the ion reflector (11).

The experimental parameters and results are presented in Table 1. An analysis of the  $^{113}\text{In}$  isotope in the 3.85-ppb target [an effective concentration of 165 parts per trillion (ppt)] has been included. A plot of relative MPRI intensity versus bulk In concentration is shown in Fig. 3. Although a logarithmic scale has been chosen for display purposes, the results of the least-squares analysis on the normalized linear plot denote a slope of  $1.00 \pm 0.01$ . In addition, the raw data from the analysis of the  $^{113}\text{In}$  in Si indicate a S/N ratio of  $\sim 9$ . If we extrapolate to  $S/N = 2$  and scale the ionization efficiency (from 0.55 to 1) (see below) and ion current (from 46 to  $100 \mu\text{A}$ ) to obtainable values for this apparatus, a detection limit of 9 ppt is obtained. Similar limits are found from a direct analysis of Fig. 3.

It is known for this type of ion-induced desorption that more than 90% of the ejecting material originates from the topmost layer of the solid (12). Furthermore, for the 165-ppt sample,  $46 \mu\text{A}$  of primary ion current was delivered to the sample in 5.6- $\mu\text{s}$  pulses. For the 5-min accumulation period, this bombardment yielded a total dose of  $1.5 \times 10^{13}$   $\text{Ar}^+$  ions into the  $0.071\text{-cm}^2$  beam spot, corresponding to a removal of  $2.0 \times 10^{13}$  surface atoms (0.29 monolayer) on the assumption that the In desorbs at the same rate (1.4 atoms per incident ion) that has been observed for Si (13). Given the detection limit of 9 ppt, this experiment is therefore sensitive to 180 atoms. If removal of an entire monolayer is required, then as few as 640 surface atoms may be detected.

The extrapolation from a concentration of 165 ppt is justified on the basis of two criteria. First, intensity versus laser power measurements have indicated a one-photon dependence in the In MPRI signal until saturation conditions are achieved (5). If saturation is assumed to correspond to 100% ionization, then we have been able to estimate the ionization efficiency of our

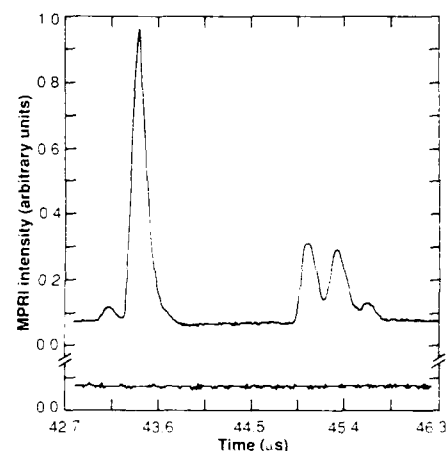
experiment to be 55%. Second, with the present ion source,  $\sim 100 \mu\text{A}$  of current can be obtained, representing approximately a twofold increase over the maximum currents used for these analyses. We have found that the measured background count does not correlate with increasing primary ion current or energy. Interestingly, the background appears to depend randomly on the sample preparation. This may be the result of significant variations in the secondary ion yields from different manipulator backing material used in these experiments.

The results presented here are made possible by several conditions. Nearly 90% of the desorbed In atoms are produced in their ground electronic state (14). Moreover, efficient resonance ionization may be achieved with relatively low laser power density. Laser beams with large spatial extent may then be used to efficiently overlap 25 to 75% of the desorbing material. Finally, the TOF analyzer offers an adequate degree of mass resolution at a transmission in excess of 10% and provides an efficient method for distinguishing the signal from the background (15). The reflector has been shown to attenuate the transmission of secondary ions by a factor of 320 because the extraction optics preferentially impart to these species a velocity greater than that of the photoions (8). We have been able to further improve this factor by accelerating the desorbed ions to even greater velocities by pulsing the target with a large positive voltage (Fig. 1). Finally, it is imperative to utilize low-intensity UV light for the resonance step to reduce the probability of ionization of gas phase or sputtered impurities that might overlap the analyte peaks in the time spectrum. The possible increase in noise associated with the use of excessive UV laser power has been documented (16).

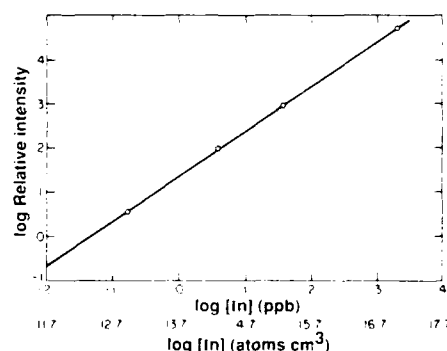
Although these experiments demonstrate that the detection of a small number of atoms on a surface is a realizable goal, a number of possible instrumental improvements might reduce our detection limits further. For example, by shortening the duration of the incident ion pulse to a few

hundred nanoseconds, it is possible to increase the fraction of desorbed atoms that intersect the photon field by more than a factor of 2. We believe that the background may be reduced by improved shielding of the target from stray ions during the time that the incident ion pulse is turned off.

The levels of detection reported here are lower by at least 100-fold than any previously reported values (7). Obviously, the preparation of standard samples with such low concentrations of analyte poses major difficulties in developing new applications that exploit the power of this methodology. It will also be necessary to fully characterize the types of species that are ejected. In some cases, formation of secondary ions, molecules, and excited states may bleed intensity from the ground-state channel (5). The analysis of the rather well-defined, high-purity Si targets in this work, however, represents



**Fig. 2.** Portion of the TOF mass spectrum obtained from the sample consisting of 2 ppm In in Si. The In isotopes are observed at  $\sim 43 \mu\text{s}$ . The other peaks in the spectrum are associated with  $\text{Cu}_2$  clusters originating from the sample holder. For comparison, the same time interval as observed with the laser blocked is shown at the bottom.



**Fig. 3.** The MPRI intensity of In versus the bulk In concentration. The In reference concentrations (in atoms per cubic centimeter) are  $1 \times 10^{17}$ ,  $1.83 \times 10^{16}$ ,  $1.92 \times 10^{14}$ , and  $8.25 \times 10^{12}$ . See Table 1 for additional information.



an important beginning for this research. A number of other novel applications also seem possible (17). For example, it appears feasible to collect a small number of atoms generated in rare nuclear decay events onto a surface. Present efforts are aimed toward determining the  $\beta\beta$ -decay half-life of  $^{136}\text{Xe}$ , a process predicted to yield annually one atom of  $^{136}\text{Ba}^{2+}$  for every  $8 \times 10^{20}$  atoms of  $^{136}\text{Xe}$  (18).

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9. The Si targets were supplied by M. Young of Hughes Research Laboratories and J. E. Parks of Atom Sciences, Inc. The wafers were prepared by liquid-encapsulated Czochralski (LEC) single-crystal growth, and the In concentrations were determined by bulk resistivity measurements. All other dopants (excluding oxygen) were present at less than  $10^{15}$  atoms per cubic centimeter.
10. Copper backing (Alpha Products, 99.999% purity) was used in the analysis of the 2 ppm In sample. The Si backing, used for the remaining measurements, was from Monsanto test grade stock (lightly boron doped, LEC grown).
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19. Supported by the National Science Foundation, the Office of Naval Research, and IBM Corporation.

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# Angular distribution of $\text{Ga}^+$ ions desorbed by 3-keV ion bombardment of GaAs(110)

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Angular distributions of  $\text{Ga}^+$  ions desorbed from GaAs(110) surfaces by 3-keV  $\text{Ar}^+$ -ion bombardment under low-dose conditions have been determined. The distributions exhibit a high degree of anisotropy along the  $\langle 100 \rangle$  crystallographic direction with smaller peaks observed in several other specific directions. Using simple geometric analyses and with microscopic insight extracted from results of molecular-dynamics computer simulations on Si(110), we have been able to identify the scattering mechanisms that give rise to these peaks. The most dominant feature is found to arise from a specific collision sequence wherein a surface atom is ejected by direct collisions with a second-layer atom along the bond direction. This mechanism is interesting in that it contrasts with the channeling and blocking mechanisms previously reported for fcc metals. The position of other peaks in the angular distributions have been determined with use of simple geometrical arguments. We also examine the expected effect of the known GaAs(110) surface reconstruction on the observed patterns. These results should prove useful for testing molecular-dynamics calculations on ion-bombarded GaAs targets and may ultimately lead to a new approach to examining the surface structure of these types of complex materials.

## I. INTRODUCTION

In recent years, there has been significant progress in understanding the interaction of keV particles with solids on an atomic scale. Experimental measurements of the energy and angular distribution of desorbed particles have been made on a variety of clean and adsorbate-covered single-crystal surfaces.<sup>1-6</sup> Detection is now possible for both secondary ions<sup>1-5</sup> and neutral atoms<sup>6</sup> desorbed by low-dose ion bombardment where surface damage is minimized. An atomic-level understanding of these interactions has been obtained through comparisons of experimental distributions and molecular-dynamics computer simulations. These calculations yield nuclear motion of the atoms in the solid, using many-body potential functions to describe the force fields.<sup>7</sup>

For ion-induced desorption from Rh(111), an fcc metal, excellent agreement between the calculated and experimental energy and angular distributions of ejected Rh atoms has been achieved using the embedded-atom method (EAM) in dynamical simulations.<sup>8</sup> An important mechanistic feature which has emerged from these and related simulations is that the ejected particles are strongly channeled and blocked by other surface atoms. These effects systematically influence the angular distributions and allow for the determination of the structure of clean and adsorbate-covered single-crystal surfaces.<sup>1-6</sup>

There have been several recent molecular-dynamics simulations performed to examine the dynamics of ion-bombarded Si crystals.<sup>9-11</sup> A basic understanding of the response of these materials to bombardment is important in explaining the characteristics of microelectronic devices constructed using ion implantation or reactive ion etching. These covalently bonded materials have been very difficult to model theoretically because of the direc-

tional nature of the bonding and also because of the dramatic reconstructions these surfaces often undergo. The latest results,<sup>9</sup> utilizing an empirically derived many-body potential, suggest that the basic mechanisms of ejection of Si atoms are quite different than the channeling and blocking mechanisms that dominate angular distributions of ion-bombarded metal surfaces. The important difference is that for Si there are large open channels where atoms can move unimpeded. In addition to the channeling and blocking mechanisms, evidence has been found for atom-atom collisions that lead to desorption along the nearest-neighbor bond directions. These simulations qualitatively support early experimental angular distributions for  $\text{Si}^+$  desorbed from ion bombarded Si(100).<sup>12</sup>

In this paper the first angular distributions of ions ejected from clean GaAs(110) under low-dose conditions are presented. At this point, accurate many-body potential have not yet been developed to describe the response of GaAs to energetic particle bombardment. From a detailed analysis of the angular distributions of  $\text{Ga}^+$  ions, however, we show that the primary mechanism of ion-induced desorption differs substantially from that observed for fcc metals. Specifically, we find that the dominant ejection mechanism involves a specific collision sequence wherein a surface atom is ejected by direct collision with a second layer atom along the bond direction. These results support the qualitative descriptions of the ion-solid interaction event obtained from molecular dynamics simulations on Si(110) and provide an important base of data for future computer simulations of the ion bombardment of GaAs. Moreover, the sensitivity of our data to the nature of the surface reconstruction suggest that these angular distributions may provide important surface structural information from rather complex systems.

## II. EXPERIMENT

All measurements were performed using an angle-resolved secondary-ion mass spectroscopy (SIMS) apparatus described elsewhere.<sup>13</sup> Briefly, the ultrahigh-vacuum (UHV) chamber was equipped with low energy electron diffraction (LEED), Auger electron spectroscopy (AES), a differentially pumped Leybold-Heraeus ion source, and an Extrel C50 quadrupole mass spectrometer (QMS). The polar angle of detection could be altered independently by rotation of the differentially pumped QMS mounting flange. The QMS was equipped with an input einzel lens with an acceptance aperture of 1.8 mm positioned 3.7 cm from the center of the experimental chamber and a 90° electrostatic sector for energy selection. This results in a total polar angular acceptance of  $\pm 3^\circ$  and a typical energy acceptance of  $20.0 \pm 0.2$  eV. The crystal manipulator allowed independent translation along three Cartesian axes and independent rotation around two perpendicular axes parallel and perpendicular to the sample surface.

There are three important angle designations of relevance to these experiments. The azimuthal angle is defined in the plane of the crystal surface, and is referenced to the  $\langle 100 \rangle$  direction on the surface as noted in Fig. 1. The incidence angle is defined as the angle between the surface normal and the ion source. The polar detection angle or ejection angle is the angle between the detector aperture and the surface normal. The three angles can be determined to a precision  $\pm 1^\circ$  and set to an accuracy of  $\pm 0.1^\circ$ . The total angular distribution is collected as a series of azimuthal angle scans at a fixed polar angle. Each scan is obtained by rotation of the sample in one-degree steps over three full revolutions. The angle positions are set by computer controlled stepping motor. For the data reported here, intensities of the various azimuthal scans, taken on different days, were normalized to a scan of the polar detection angle. Azimuthal scans

were not corrected for the increase in azimuthal acceptance as the polar detection angle was decreased. This effect results in azimuthal acceptances of  $3.3^\circ$  and  $1.5^\circ$ , at polar angles of  $25^\circ$  and  $70^\circ$ , respectively.

Undoped, semi-insulating GaAs(110) wafers were obtained from M/A Com Laser Diodes. The wafers were cleaved into pieces and degreased in trichloroethane, acetone, ethanol, and methanol before etching in a 1:1:5 solution of peroxide:water:sulfuric acid. The (110) face was found to be oriented within  $\pm 0.5^\circ$  by Laue x-ray diffraction. Each sample was attached with In to a Mo block which was mounted onto the manipulator. Sample heating was provided by an electron bombardment source located behind the Mo block.

All surfaces were prepared by cycles of ion bombardment and annealing to  $585^\circ\text{C}$  for 2 min. This procedure provided a clean and ordered surface as determined by LEED, AES, and SIMS. The total ion dose during experiments was maintained at static levels by limiting the exposure time to less than one-tenth of the time required to desorb one monolayer of GaAs. This was accomplished by focusing a 2-nA beam into a 1-mm spot located 3 mm from the rotation axis of the crystal. During an azimuthal scan the entire wafer was slowly rotated through three full  $360^\circ$  revolutions over a time of about 45 min. To ensure that the crystal edges were playing no role in the observed features, experiments were carried out on two crystals of vastly different shapes. No distinguishable differences in the patterns could be discerned. We were only successful at detecting the Ga<sup>+</sup> ions under static conditions. The incident ion flux had to be increased to unacceptable levels to achieve any discernible As<sup>+</sup> signal.

Ion collection over three full rotations served several purposes. First, the influence of beam damage could be minimized and carefully monitored since a virgin area of the crystal was constantly being exposed to the beam. Second, the data could be conveniently averaged. Final-

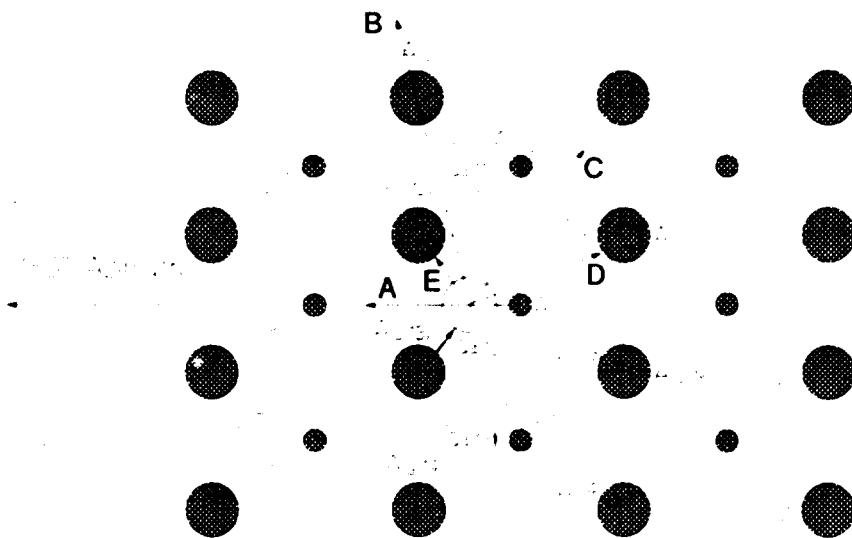


FIG. 1. The structure of the unreconstructed GaAs(110) surface. The open and hatched circles represent Ga and As atoms, while the larger and smaller circles represent atoms in the first and second layers, respectively. The arrows indicate the various channeling and blocking directions suggested by this structure.

ly, each scan could be set to begin at the same azimuth at which the previous scan had ended. This feature provided a consistent reference of the azimuths between scans of different polar angles even for dramatically different patterns.

### III. RESULTS AND DISCUSSION

The angular distribution of  $\text{Ga}^+$  ions ejected from  $\text{GaAs}(110)$  is shown in Fig. 2. As seen in the figure the distribution could be obtained at each azimuthal angle between  $0^\circ$  and  $360^\circ$  for a series of polar angles between  $25^\circ$  and  $70^\circ$ . These data are clearly characterized by a high degree of symmetry and anisotropy. The striking feature of our results is the single, intense  $\text{Ga}^+$  ion peak observed at a polar angle of  $35^\circ$  and at an azimuthal angle of  $180^\circ$ . Other features are positioned with nearly mirror plane symmetry about this major peak. At higher polar angles, other maxima and minima are observed at various azimuthal angles. It is our goal to associate these anisotropies with the known surface structure of  $\text{GaAs}(110)$  and hence to determine the mechanistic details of the ion-solid interaction.

The atomic structure of the bulk terminated  $\text{GaAs}(110)$  surface is shown in Fig. 1. The surface chain appears as a vertical zigzag row of alternating As and Ga atoms. The second-layer atoms, as denoted by the smaller circles, are positioned with a similar geometry. It has been known from LEED measurements<sup>14</sup> that the surface reconstructs extensively by a bond length conserving surface chain rotation of  $\sim 29^\circ$ . More specifically, reconstruction involves the movement of surface Ga atoms into the crystal

surface, and away from the second layer As atoms, while the movement of the surface As is out of the surface, and toward the second layer Ga atoms. This structure has been verified independently by a variety of techniques including angle-resolved photoemission,<sup>15,16</sup> isochromat spectroscopy,<sup>17,18</sup> medium energy ion scattering,<sup>19</sup> and shadow cone enhanced SIMS.<sup>20</sup>

The most prominent features of the angular distribution shown in Fig. 2 can be explained in a rather straightforward fashion if it is assumed that the most favorable  $\text{Ga}^+$  ion ejection mechanism involves direct atom-atom collisions along the bond directions. For example, the pronounced peak in the  $\text{Ga}^+$  ion distribution at  $\theta = 35^\circ$  and  $\phi = 180^\circ$  would arise from collisions between the second-layer As atom, As(22), and the surface Ga atom, Ga(12), along the direction of their common bond. The mechanism is illustrated with arrow A shown in Fig. 1. Note that no such mechanism is possible along  $\phi = 0^\circ$ , accounting for a lack of significant signal along this azimuth. As we shall see, several other peaks in the distribution may also be explained in a straightforward fashion.

To more quantitatively interpret the origin of the features apparent in Fig. 2, it is really necessary to perform computer simulations of the ion-impact event. Unfortunately, classical dynamics computer simulations are not yet available for  $\text{GaAs}$  crystals to help us with this problem. There have been recent attempts, however, to determine the angular distributions of Si atoms ejected from the  $\text{Si}(110)$  surface.<sup>9,10</sup> It is feasible to utilize these calculations in making assignments of at least the most prominent features in the angular distributions measured

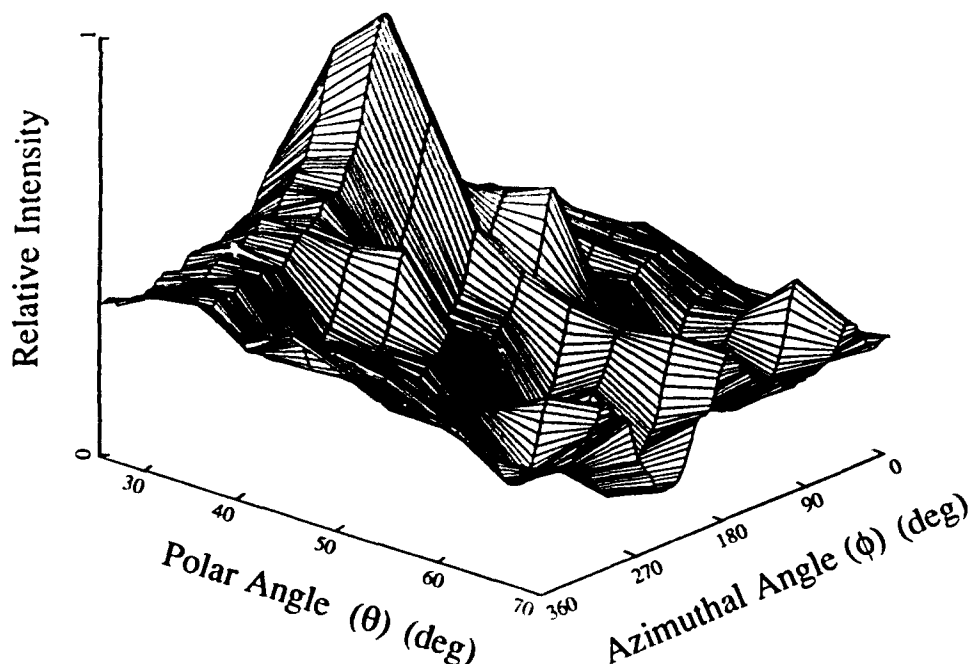


FIG. 2. The ion-induced angular distribution of  $\text{Ga}^+$  ions desorbed by 3-keV normal incident  $\text{Ar}^+$  ion bombardment of  $\text{GaAs}(110)$ . The polar angle refers to the angle of detection from the surface normal. The azimuthal angle is referenced to the  $\langle 100 \rangle$  direction on the crystal surface. The energy of the ions detected was  $20.0 \pm 0.2$  eV, and the distribution is shown for a fixed total angle of acceptance.

from GaAs. The bulk crystal structure of the two materials is, of course, closely related. Moreover, previous calculations of these distributions have shown that the response of a solid to keV ion bombardment is influenced more strongly by structure than by chemical bonding forces.<sup>1-4,7</sup> The same basic azimuthal angle distribution is found for Cu(111)<sup>1</sup> and for Rh(111),<sup>6</sup> for example, even though there may be small differences in the relative intensities of the maxima and in the values of the angles associated with the peaks in the polar angle distributions. The calculated distribution of Si atoms ejected from an artificial bulk-terminated Si(110) surface with kinetic energies between 10 and 30 eV is shown in Fig. 3. This plot was obtained from the calculated distribution of Si atoms by selecting only those ejected atoms that would be Ga atoms in the GaAs(110) crystal.

This distribution yields surprisingly good agreement with the experimental distribution of Fig. 2. A single, prominent peak is found at  $\theta = 38^\circ$  and  $\phi = 180^\circ$ . Even the smaller features near  $\phi = 90^\circ$  and  $270^\circ$  at  $\theta > 50^\circ$  also seem to have a tentative correspondence with the experimental data. The computer simulations clearly show that a significant number of ejected atoms that make up the peak along  $\phi = 180^\circ$  arise from ejection of a surface Ga atom by the direct collision of a second-layer As atom along the direction of their common bond.<sup>9</sup>

This type of mechanism is quite different than that discussed for the ejection of metal atoms from single crystal metal surfaces. For metals, the most important origin for the angular anisotropies arises from channeling and blocking of the ejecting first-layer atoms by other surface atoms. Atom-atom collisions contribute only a small in-

tensity to the distributions. For example, the Rh(111) surface with two different threefold symmetric open azimuthal directions only displays a 20% enhancement in the neutral atom ejection yield along the "hcp" direction.<sup>18</sup> The classical dynamics simulations reveal that this effect is due to a specific collision sequence of second-layer atoms colliding with surface-layer atoms and ejecting them along their bond directions. Thus, there is precedence for the contribution of atom-atom collisions to the ejection process, although it appears to be much more important in covalent crystals such as Si and GaAs.

It is instructive to quantitatively compare the experimental and calculated values of the polar angle of maximum intensity. We believe it is reasonable to make this comparison even though we have chosen to detect Ga<sup>+</sup> ions in the SIMS mode rather than neutral Ga atoms. Preliminary experimental polar angle distributions along  $\phi = 180^\circ$  for the neutral distribution as obtained with a multiphoton resonance ionization detection scheme,<sup>21</sup> and for Ga<sup>+</sup> ions, is shown in Fig. 4. Both distributions peak at the same polar angle and exhibit the same general features. Apparently, in this kinetic energy regime, there is only a minimal effect of angle-dependent ionization probabilities and of the image potential, in contrast with what has been observed from metal surfaces.

As noted above, the Si yield along  $\phi = 180^\circ$  maximizes at a polar angle of  $38^\circ$ . If the desorption of Si occurred directly along the bond direction, it would be expected to occur at  $\theta = 35^\circ$ , obviously very close to the calculated value. Both of these values are obtained for a bulk-terminated Si(110) surface. For our experiments on

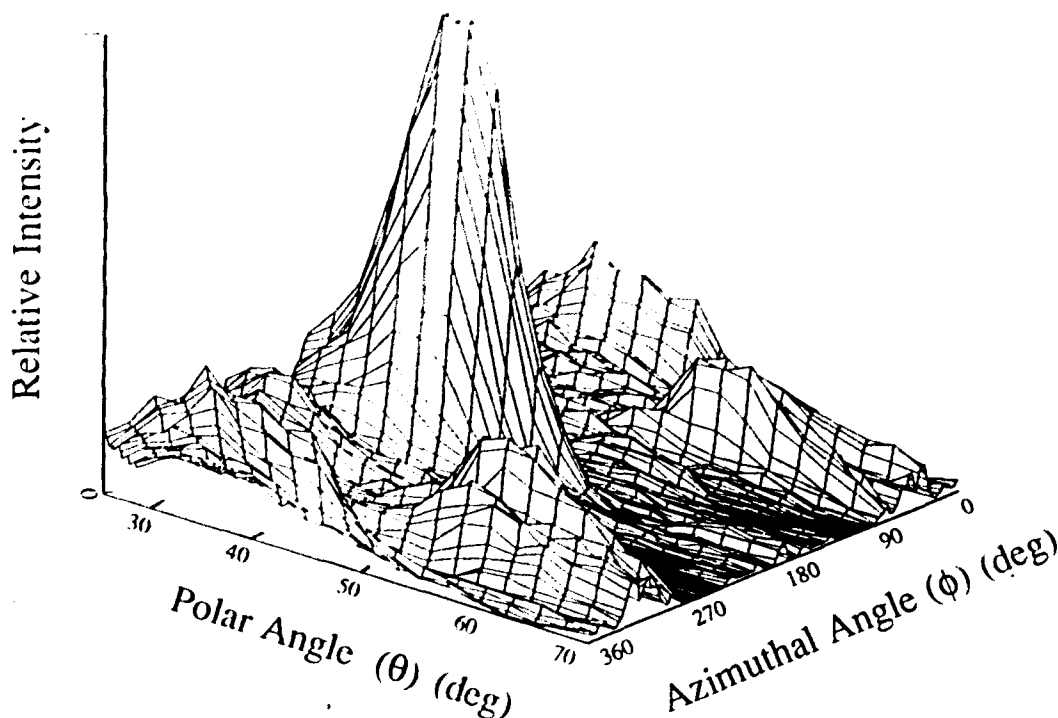


FIG. 3. The calculated angular distribution of secondary Si atoms, with kinetic energies between 10 and 30 eV, desorbed from Si(110) by 1-keV Ar<sup>+</sup> ion bombardment. The angular distribution is shown with reduced symmetry to allow for the direct comparison with the experimental Ga<sup>+</sup> ions distributions for Ga<sup>+</sup> ions desorbed from GaAs(110).

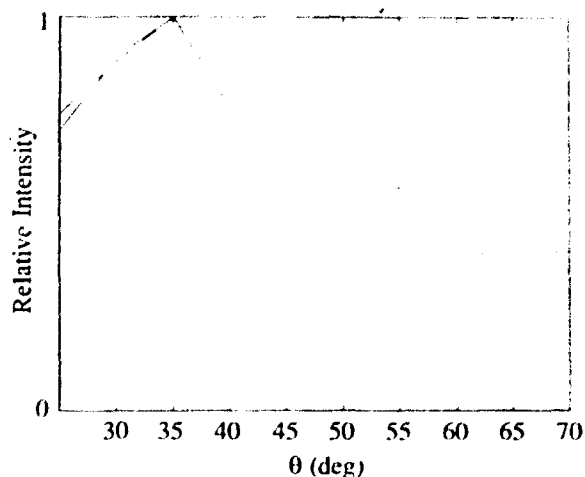


FIG. 4. The polar distribution of 20-eV Ga<sup>+</sup> ions (solid line) and Ga atoms, with kinetic energies between 20 and 50 eV (broken line) desorbed from GaAs(110).

GaAs(110), the peak in the polar angle along  $\phi=180^\circ$  is also observed at  $\theta=35^\circ$ . For this system, however, the topmost Ga atom moves downward by 0.50 Å and the topmost As atom moves outward by 0.15 Å. This chain rotation increases the As(22)—Ga(22) bond angle to  $44^\circ$  with respect to the surface normal, a value nearly  $10^\circ$  larger than that found experimentally. The difference presumably arises by distortions created by As(12) and As(13). After the reconstruction they are in a position to focus ejecting Ga atoms closer to the surface normal. In future experiments and simulations, it will be interesting to see if such distortions are, in fact, quantitatively calculable. Such measurements would provide a straightforward procedure for determining a number of rather subtle surface structures.

Finally, the Si computer simulations suggest that a significant portion of the intensity in this major peak may consist of Ga<sup>+</sup> ions ejected from the second layer which are focused into this same angular region.<sup>9</sup> It is not possible for us to experimentally distinguish between first and second-layer Ga<sup>+</sup> ions. At this point, then, we cannot confirm this intriguing prediction of the computer simulations.

The next set of structurally significant features apparent from the distributions shown in Fig. 2 occur at an exit angle of  $\theta=45^\circ$ . The azimuthal angle distributions are shown in Fig. 5. For this case, an additional pair of peaks is observed at  $\phi=102^\circ$  and  $\phi=252^\circ$ . This structure could potentially originate from a large group of channeling mechanisms. The computer simulations on Si, however, show that these features arise mainly from the ejection of Ga(12) through the channel created by As(12) and Ga(11). Assuming that the particles move midway between As(12) and Ga(11), this direction is expected to be found at  $76^\circ$  on either side of the  $\phi=180^\circ$  azimuth at  $\phi=104^\circ$  and at  $\phi=256^\circ$ . These predictions are in close agreement with the peak positions shown in Fig. 5. The channeling direction is denoted by arrow B in Fig. 1 and the relevant angles are summarized in Table I. We suspect that this mechanism is made somewhat more

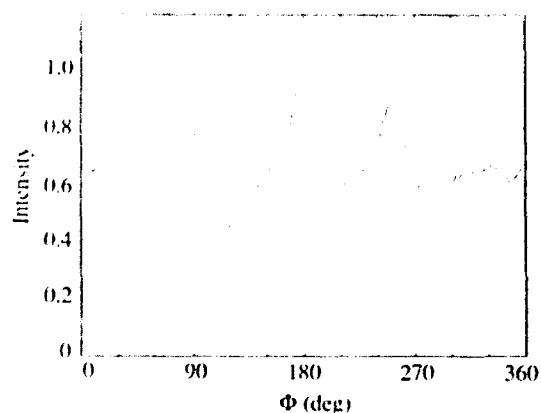


FIG. 5. The relative intensity of 20-eV Ga<sup>+</sup> ions desorbed from GaAs(110) as a function of azimuthal angle at a polar angle of  $45^\circ$  from the surface normal.

favorable by the fact that As(12) is moved up and out of the surface plane of the reconstructed surface, hence opening the channel slightly. The calculated distribution again shows a component of second-layer atoms in this peak, and thereby justifies consideration of their possible contribution to the intensity of these peaks. However, no specific mechanism leading to the focusing of second-layer atoms into these peaks can easily be found.<sup>9</sup> The fact that the experimental azimuthal spectra do not exhibit perfect experimental mirror plane symmetry about  $180^\circ$  azimuth is presumably a manifestation of unknown imperfections in the GaAs(110) crystal surface. These small asymmetries are only apparent at polar angles greater than  $40^\circ$ , angles where these effects might be expected to most strongly influence the results.

A similar azimuthal angle distribution is obtained at  $\theta=65^\circ$  as shown in Fig. 6. In this case, however, a small peak at  $\phi=0^\circ$  is observed, presumably due to channeling of Ga(12) along this direction after it has received momentum from lattice atoms moving in random directions. Moreover the computer simulations show that by As(15) and As(16) the channeling mechanism B is no longer possible. Instead, Ga(12) is ejected by As(13) after the latter has been driven down into the crystal. For metal surfaces, this has been referred to as the "up-down" mechanism, and it generally propagates through a close-packed row. The GaAs lattice is much more open, so Ga(12) may escape directly along the As(13)—Ga(12) bond axis. This mechanism is denoted by arrow C in Fig. 1 and should occur at  $\phi=55^\circ$  and  $\phi=305^\circ$  as summarized in Table I. Note that the experimental values of  $\phi=52^\circ$  and  $\phi=306^\circ$  are in close agreement with this assignment.

Two sets of minima are apparent in Fig. 6. The first set is seen at  $\phi=26^\circ$  and  $\phi=334^\circ$  and is due to blocking of Ga(12) by As(15). The second set is seen at  $\phi=116^\circ$  and  $\phi=237^\circ$  and is due to blocking of Ga(12) by As(12). The mechanisms are denoted by arrows D and E, respectively, and are also summarized in Table I.

In general, there is close agreement between the positions of the peaks and valleys of the azimuthal distributions as expected from simple trigonometric arguments

TABLE I. Comparison of calculated and measured channeling and blocking features on GaAs(110).

Mechanism <sup>a</sup>	Calculated <sup>b</sup>	Fig.	Measured	Type	Observed as
<i>A</i>	0°	6	0°	Channeling	Maximum
	180°	2, 5, 6	180°		
<i>B</i>	104°	5	102°	Channeling	Maximum
	256°	5	252°		
<i>C</i>	55°	6	52°	Up-down	Maximum
	305°	6	306°		
<i>D</i>	25°	6	26°	Blocking	Minimum
	335°	6	334°		
<i>E</i>	123°	6	116°	Blocking	Minimum
	235°	6	237°		

<sup>a</sup>See Fig. 1 for the definition of these mechanisms.<sup>b</sup>Azimuthal angle  $\phi$  calculated from simple trigonometry as indicated in Fig. 1 and in the text.

without including the influence of the GaAs(110) surface reconstruction on these distributions. The net effect of the reconstruction is to shorten the lateral spacing of the surface Ga and As atoms, thereby increasing the expected angular spacing of the blocking features. The chain rotation of 29° results in a change of the predicted positions of the appropriate maxima and minima by only about 3°. This small difference is really beyond the error limits of our simple models. Moreover, at this stage it is not completely clear how to assign a specific angle to a blocking feature. In the absence of any model of the shape of these features, the blocking angle was arbitrarily determined at the intensity minima. Other scenarios for picking this angle are equally likely. For instance, along the 180° azimuth it can be seen that inner edges of the As atoms are quite close to the ejecting Ga atoms. These ejecting atoms are likely to interact strongly with both surface As atoms. This three-body interaction would result in intensity distributions whose edges near the 180° azimuth are displaced away from the azimuth, resulting in error. We believe that both the surface reconstruction and distortions due to the blocking atoms are playing a role in the quantitative discrepancy observed along the 180° azimuth, but the qualitative agreement certainly

supports our assignments.

The anisotropy observed at  $\theta=45^\circ$  is extremely sensitive to ion damage of the surface. The ion yield at a 45° degree angle of detection under two different ion fluxes is shown in Fig. 7. The solid line shows the ion yield with a beam current of 1.6 nA while the dotted line is the ion yield of the next consecutive scan where the beam current has been increased to 5.5 nA. These data demonstrate not only the reproducibility of the three peaks observed along the 180° azimuth, but also the decay of signal as a function of ion dose. It should be noted that the curve at lower ion fluence shows no significant decrease in peak intensity over the three revolutions, while the high fluence curves shows a continuous decrease in signal intensity. The patterns of desorption from surfaces having sustained a significant amount of ion-induced damage have also been determined, and differ drastically from those of ordered surfaces. For instance, the pattern at 45° angle of detection from a heavily damaged surface, seen in Fig. 8, shows only one broad peak at the 180° azimuth

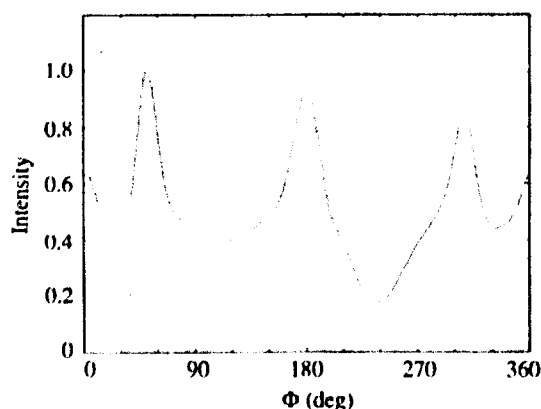


FIG. 6. The relative intensity of 20-eV  $\text{Ga}^+$  ions desorbed from GaAs(110) as a function of azimuthal angle at a polar angle of 65°.

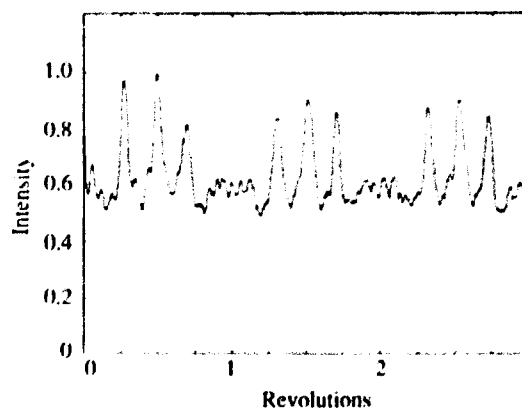


FIG. 7. The relative intensity of 20-eV  $\text{Ga}^+$  ions desorbed from GaAs(110) obtained during three complete revolutions of the crystal at a polar angle of 45° with ion beam currents of 1.6 nA (solid line) and 5.5 nA (broken line). The intensity of the distribution at 1.6 nA has been multiplied by 3.6 to provide for the direct comparison of the two curves.

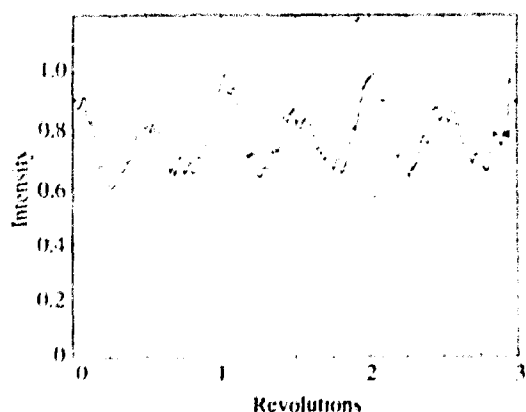


FIG. 8. The relative intensity of 20-eV Ga<sup>+</sup> ions desorbed from an ion beam amorphized GaAs(110) surface obtained during three complete revolutions of the crystal.

in contrast with the three sharp peaks observed from an ordered surface.

The sensitivity of the characteristic three-peak pattern of the azimuthal distribution at a polar angle of 45° was exploited as an *in situ* monitor of ion-induced damage. After each cycle of ion bombardment and annealing, an azimuthal scan at a polar angle of 45° was collected. The resulting anisotropy was used as the criterion for continuing the experiment by changing the polar angle of detection and collecting more azimuthal spectra or terminating the experiment due to poor surface order. Also, at the end of each series of experiments a scan of the azimuthal distribution at a polar angle of 45° was acquired to judge the cumulative effect of the total ion dose.

A few final aspects of the angular distributions deserve further discussion. First, in each azimuthal spectra there exists a significant baseline signal. This signal is believed to be due to disordered areas of the surface generated by either the ion bombardment or annealing. In Figs. 2 and 6, the intensity minima around the 180° azimuth do not dip to zero signal levels and are, in fact, unequal in intensity. The failure to drop to zero intensity is also attributed to disordered areas of the surface, while the unequal intensities may arise from the presence of regions of the surface with an overlayer of metallic Ga. We believe that this overlayer exists as a "raft" similar to that formed by Al (Ref. 22) and is always present after ion bombardment or heating.

#### IV. CONCLUSION

We have presented, for the first time, the angular distribution of Ga<sup>+</sup> ions desorbed from the GaAs(110) sur-

face by 3-keV Ar<sup>+</sup> ion bombardment. From a simple geometric analysis of the ion-induced desorption pattern, we find that the mechanism of ion ejection from this surface is drastically different from the blocking and channeling observed previously on metal surfaces.<sup>1,6</sup> Specifically, the ejection of Ga<sup>+</sup> ions into a single peak, at 35° from the surface normal and along the 180° azimuth, dominates the distribution and is attributed to a direct ejection mechanism in which a second layer As atom collides with a surface Ga atom, causing it to desorb along their common bond direction. Although the geometric analysis provides an excellent qualitative explanation of the observed desorption pattern, some quantitative disagreements remain between the geometric analysis and the observed distribution. The development of a suitable potential for use in full dynamics calculations of the ion bombardment of GaAs should allow for the resolution of the uncertainties that exist in the analysis and provide for the accurate determination of surface structures from the angular distributions of ion-induced secondary ions.

We believe that this work has demonstrated that the angular distribution of secondary ions contains a wide variety of information about both the surface structure and the mechanisms of momentum transfer which result in ion desorption. The results not only serve to increase our understanding of the ion-solid interaction itself, but also suggest that angle-resolved SIMS may become a unique tool for the characterization of a wide variety of complex structures associated with semiconductor surfaces. Of particular interest is the study of molecular beam epitaxially grown GaAs(100) which displays a number of surface reconstructions. These surfaces can be prepared in our growth chamber and transferred under UHV conditions to our analysis chamber.

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